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CRF NEWS

Celebrating 25 Years 1979–2004

COMBUSTION RESEARCH FACILITY

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Instruments used elsewhere: CRF technologies in the real world

This article by contributing writer Emmeline Chen continues a series commemorating the CRF's 25th anniversary.

Throughout the past 25 years, CRF scientists have developed innovative instruments and techniques to address particularly difficult issues in the combustion industry. CRF researchers with expertise in many different disciplines have successfully teamed with companies to better understand and analyze technical problems and processes. Here are a just a few of the promising devices and technologies emerging from the CRF that demonstrate potential impact beyond the laboratory.

Detecting gas leaks

Gas leak detection in the United States and Japan may soon be easier, thanks to the CRF's development of two portable imagers: a hydrocarbon leak detector for use in petroleum refineries and a natural gas (methane) imaging system.

Both systems use a technique called backscatter absorption gas imaging (BAGI) to illuminate a scene with infrared (IR) laser radiation. Any target gases present in the scene absorb the laser light, creating dark clouds in the video image of an IR camera.

Tests at petroleum refineries in California, Texas, and the United Kingdom showed the hydrocarbon imager to be a promising alternative to the laborious gas leak detection technique currently mandated by the Environmental Protection Agency.

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Sandia National Laboratories

CRF scientists develop experimental database for sooty diffusion flames

Efforts to minimize the dangers of pool fires—caused by spills of aviation fuel—can now draw from a new resource: an experimental database filled with laser-based and extractive measurements of critical parameters in sooty diffusion flames.

The database, which was completed by researchers at the CRF and in Sandia/New Mexico's Fire Science and Technology group, supports the construction and testing of soot formation and radiation models in diffusion flames. Such models are needed for a multiphysics pool-fire simulation code being developed at Sandia because thermal radiation from high-temperature soot is the dominant mode of heat transfer from pool fires to other objects, such as cargo being shipped.

The research team for this project led by Chris Shaddix included Pascale Desgroux from the University of Lille, France, and Sandians Tim Williams (postdoc), Bob Schefer, Linda Blevins, Bob Harmon, Matt Boisselle, Al Salmi, Doug Scott, Jill Suo-Anttila, Kirk Jensen (postdoc), Sean Kearney, and Nancy Yang.

Types of fuels and flames

Researchers investigated three fuels burning in air: methane, ethylene, and a six-component JP-8 military jet fuel surrogate developed at the University of Utah.

They established steady and pulsed laminar flames in both slot and coannular-flow configurations. The unsteady flames allowed the interrogation of flame–vortex interactions and their effects on soot formation and radiation. Researchers also performed some measurements in "inverse" slot flames, where a deficient amount of air is provided to the central slot, surrounded by excess fuel gas. Normal and inverse slot flames are shown in Figure 1, along with a slot burner.

For the JP-8 surrogate flames, a small, capillary-driven ceramic flash vaporizer was used to vaporize the fuel mixture at the burner base without fuel-distillation or thermal-cracking effects.

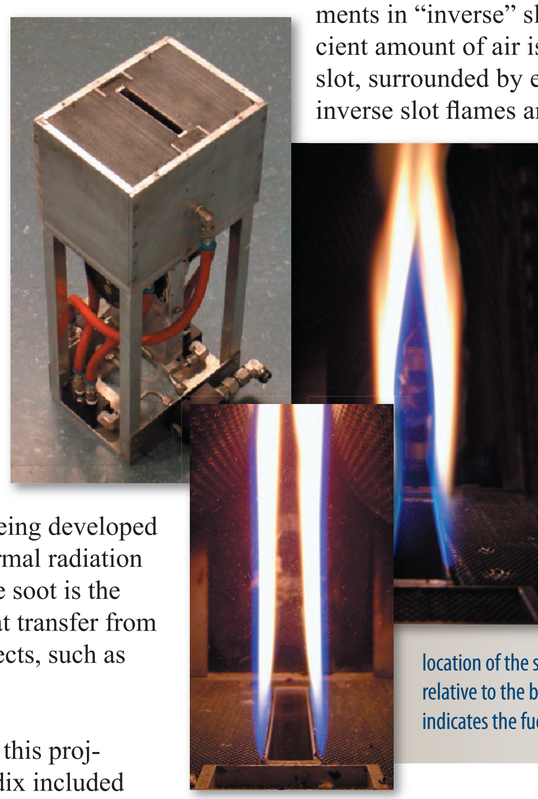


Figure 1. A slot burner (left) used to create slot flames of methane burning in air in normal (center) and inverse (right) configurations. Note the location of the soot (yellow luminosity) in the two flames relative to the blue CH* chemiluminescence, where CH* indicates the fuel-rich edge of the flame sheet.

Critical measurements

The team used a variety of methods to measure critical parameters in the sooty diffusion flames.

Hydroxyl (OH) radicals and polycyclic aromatic hydrocarbons (PAHs) were imaged using planar laser-induced fluorescence (PLIF), while tunable diode laser absorption spectroscopy measured acetylene and water vapor. The flame velocity fields were determined by particle image velocimetry.

(Continued on page 6)

Imaging of advanced low-temperature diesel combustion

Diesel engine developers are exploring many novel alternative combustion strategies for diesel engines to try to satisfy impending emissions regulations. These new strategies generally use increased pre-combustion fuel-air mixing and/or aggressive exhaust gas recirculation (EGR) to achieve low-temperature combustion (LTC). Unfortunately, LTC strategies can create other problems, such as increased unburned fuel and carbon monoxide (CO) emissions, as well as efficiency and control penalties. The in-cylinder mechanisms responsible for the problems of these new LTC conditions are not yet well understood.

By contrast, conventional diesel combustion processes are relatively well known, due in large part to the contributions of the CRF. Over the past 15 years, CRF researchers have applied multiple optical laser/imaging diagnostics to study in-cylinder processes, leading to a conceptual model for conventional diesel combustion that has become an industry-wide standard in describing conventional diesel combustion (see *CRF News* July/August 2004). Sandia researchers are now working to extend this model to describe in-cylinder processes for LTC diesel conditions.

Recently, Sandians Mark Musculus and David Cicone used a suite of optical diagnostics to examine in-cylinder liquid spray, mixing, fuel vaporization, ignition, combustion, and pollutant formation processes of one representative low-sooting LTC operating condition in the Sandia/Cummins optical heavy-duty diesel engine. The engine was operated with a single early fuel-injection event and with 12.7% (v/v) intake oxygen to simulate EGR so that NO_x emissions were very low and in-cylinder soot was almost completely eliminated. Using two cameras with appropriate filters and a beam splitter, they combined optical diagnostics in various pairings to study interactions between in-cylinder processes. These observations are summarized in Fig. 1.

As shown in image 1 of Fig. 1, because of the low ambient temperature and density for the early-injection condition, the liquid fuel (blue) penetrates nearly 50 mm before a clear separation from the vapor-fuel perimeter (green) becomes evident, compared to about 25 mm for conventional diesel combustion. Traveling longer penetration lengths, the liquid fuel may impinge on and wet in-cylinder surfaces, potentially degrading combustion efficiency and emissions.

A few crank angle degrees later, shown in images 2 and 3, chemiluminescence emission from ignition reactions (green) envelopes the liquid fuel (blue) and the ignition energy release contributes to vaporization of liquid fuel observed at the end of fuel injection. Then, in image 4, as the subsequent premixed burn commences, OH fluorescence (green) fills the laser sheet, indicating near-stoichiometric mixtures throughout much of the jet cross section. In contrast, a conventional diesel jet is typically fuel-rich, and OH in the diffusion flame is confined to a stoichiometric shell on the perimeter of the jet.

Finally, laser-induced incandescence of soot (red, image 5) and soot luminosity (red, image 6) show that soot forms exclusively at the head of the jet, in regions that are deficient in OH (green). Because soot only forms in fuel-rich regions, its presence indicates that mixing is least complete in the head vortex region of the jet and that the following "steady" jet is more well-mixed than the head. Using these and other observations, Dec's 1997 conceptual model (see *CRF News* September/October 1997) for conventional diesel combustion has been extended to include these features for this early-injection, LTC diesel condition.

Other LTC strategies with different fuel-injection schedules are also being examined. In collaboration with Ph.D. student Satbir Singh and Prof. Rolf Reitz of the University of Wisconsin, the predictive capability of multidimensional computational fluid dynamic computer models for in-cylinder LTC processes will be improved, using experimental data from Sandia for validation. Also, Musculus and Lachaux are now developing new diagnostics to study the genesis of unburned fuel emissions for LTC modes.

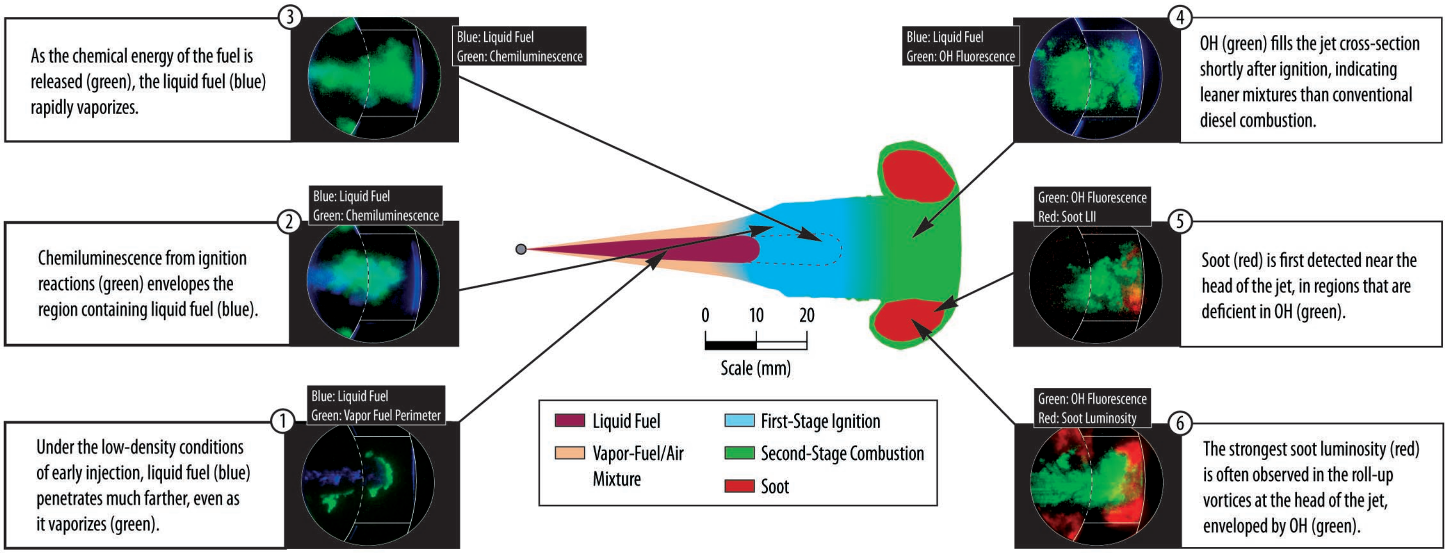


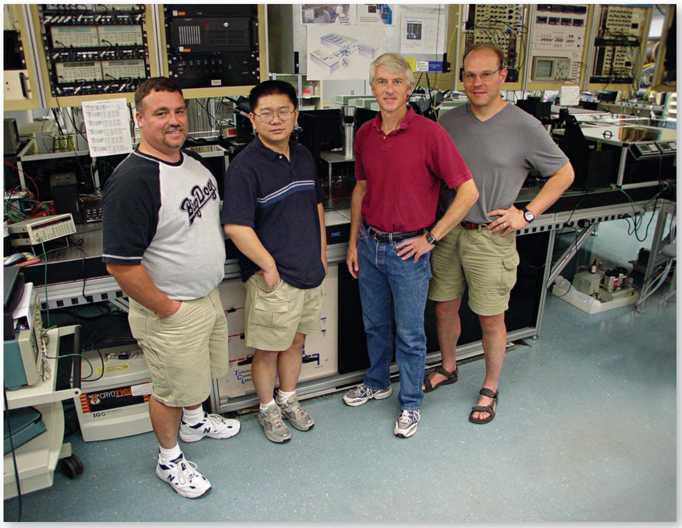
Figure 1. Schematic of the extended conceptual model of diesel combustion, along with selected simultaneous optical diagnostic images from low-temperature combustion.

Bob Carling

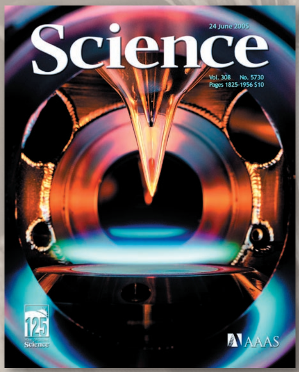
Robert W. Carling is the new Director of Center 8700, Physical and Engineering Sciences. Prior to that, Carling served as manager of chemical sciences. With a Ph.D. in physical chemistry, he started at Sandia in materials research and has worked at the CRF since 1986, becoming a senior manager about five years ago. Carling said he enjoys “putting teams of people together to work on really hard problems of national importance, worthy of a national lab.”

Dirk Geyer

Dirk Geyer from the Technical University of Darmstadt visited the CRF during the week of August 8. Working with Rob Barlow and Guanghua Wang (Sandia postdoc), he analyzed experimental results of scalar dissipation in flames. In 2004, Geyer visited the Turbulent Combustion Laboratory, where Bob Harmon is the lead technologist.



Left to right: Bob Harmon, Guanghua Wang, Rob Barlow, and Dirk Geyer.



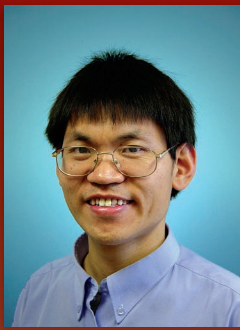
CRF researchers demonstrate existence of enols

An international team including CRF scientists demonstrated that enols, a class of molecules missing from current oxidation models, occur in a wide range of hydrocarbon flames. The research, published in the June 24 issue of *Science* (see Molecular Beam Mass Spectrometry for links to the published paper), can potentially impact prevailing hydrocarbon oxidation mechanisms, from understanding and reducing pollutant formation in combustion to describing partial oxidation in fuel cells. The team that discovered the enols included CRF researchers Craig Taatjes, Nils Hansen, Andrew McIlroy, Jim Miller, Stephen Klippenstein, and Juan Senosiain, as well as scientists from Cornell University of Massachusetts, the University of Bielefeld (Germany), and the National Synchroton Research Laboratory in Hefei, China.

Linda Canaan heads CRF visitor program

Linda Canaan joined CRF as administrator for the Visitor Program in July 2005. A lawyer who formerly practiced immigration law, Canaan will be supervising the program that brings in corporate and academic visitors as well as students.

Xiangling Chen



Postdoc Xiangling Chen left the CRF in July after accepting a position at Checkpoint Technologies, LLC in San Jose, CA. Xiangling had worked with Tom Settersten since December 2002 on the development of picosecond two-color resonant four-wave mixing spectroscopy to study molecular collisions in flames (see *CRF News* May/June 2003).

Internships at the Physical Sciences Institute

CRF's Physical Sciences Institute (PSI) graduate and undergraduate interns delve into physical-science problems with Sandia mentors. This year's program participants included Mark Dansson, Chip Humphries, Sachin Desai, Elliott Schmitt, Michael Boutross, Eric Hall, Sarah Iams, Huseifa Ismail, Alex Murray, Adam Knepp, Ethan Hecht, Carl Mas, PapaMagatte Diagne, Mark Wiley, Jennifer Freitas, Andrea Hansen, and Lizz Harpell. Their projects included the following:

- Huseifa Ismail is using laser photolysis and infrared laser frequency-modulation spectroscopy to measure product formation in reactions of alkyl radicals with molecular oxygen.
- Adam Knepp is helping to measure the kinetics of elementary reactions of the vinyl radical, an important intermediate in hydrocarbon combustion and in the chemistry of planetary atmospheres, using laser photolysis and visible laser absorption.
- PapaMagatte Diagne has led the effort to develop a computer interface for a suite of instruments to measure fiber laser performance using LabView, an industry-standard software package.
- Michael Boutross has been involved in flame modeling.
- Ethan Hecht is working on developing solid-oxide fuel cell membranes and electrodes for the selective partial oxidation of light hydrocarbons.
- Mark Wiley has developed new software for the analysis of diesel spray combustion.
- Eric Hall wrote Java visualization software that allows the CRF to share low-pressure flame data with collaborators through the internet.
- Sachin Desai is investigating in-cylinder combustion processes in a direct-injection, hydrogen-fueled internal combustion engine using OH* chemiluminescence.
- Carl Mas applied Sandia's system-modeling environment (H2Lib) to simulate distributed power generation at the Hawaii Natural Energy Institute's hydrogen energy park.
- Elliott Schmitt applied Sandia's system-modeling environment ('H2Lib') to simulate distributed power generation at DTE's Hydrogen Technology Park.

Prospective interns can apply as early as this fall. At http://education.ca.sandia.gov/internships/index.lhtml

Reminder: CRF tech symposium

The CRF's 25th Anniversary technical symposium, "Fueling America's Engine: Clean, Efficient Use of Fuels," will take place on November 17th, 2005 at Sandia Laboratories in Livermore, CA. Speakers will include: Marilyn A. Brown, director, Energy Efficiency, Reliability and Security at Oak Ridge National Laboratory; Alan C. Lloyd, secretary, California Environmental Protection Agency (EPA), Margo T. Oge, director, Office of Transportation and Air Quality, EPA; and Paul Roberts, Journalist, author of "*The End of Oil: on the Edge of a Perilous New World*, and contributor to *Harpers Magazine*.

Celebrating 25 Years 1980–2005

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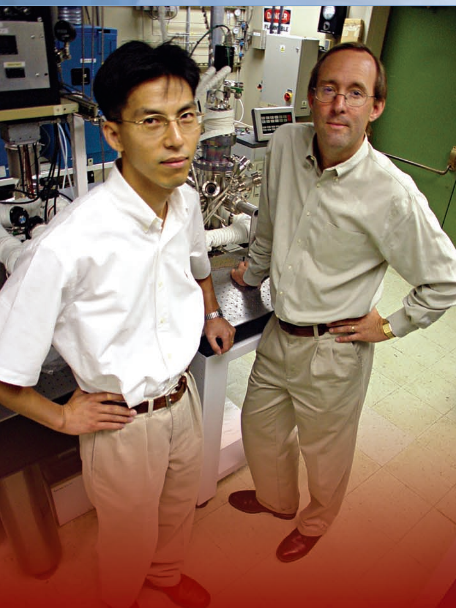


Yong Kee Chae

Postdoc Yong Kee Chae (left) has accepted a position at Applied Materials in Santa Clara, CA, where he will be looking at the formation of silicon dioxide thin films for liquid crystal display keys. While at Sandia, Chae worked with Tony McDaniel on characterizing novel hydrogen materials in the form of complex metal hydrides, and Mark Allendorf (right) on the chemical vapor deposition of tin oxide on float glass.

Ansis Upatnieks

Postdoc Ansis Upatnieks left the CRF on July 29th to join General Motors R&D in Detroit, MI where he will be working with Dr. Paul Najt. At the CRF, Upatnieks worked with Chuck Mueller, researching nontraditional fuels for low-temperature combustion.

Instruments *(Continued from page 1)*

Checking for gas leaks; the unseen is made visable.

The methane detector, developed under the sponsorship of the Japan Gas Association, also performed well in tests at the Tokyo and Osaka Gas safety facilities. This instrument improved upon previous sensors by using two wavelengths—one absorbed by methane and one that is not—for illumination and then calculating the logarithmic ratio of wavelength absorption for each pixel of the video image. The resulting picture eliminates background items, providing a clear view of any methane gas leaks.

Tom Kulp, Ricky Sommers, and Sal Birtola contributed to the development of both imaging systems. The hydrocarbon detector team also included Karla Armstrong and Dahv Kliner, while Ray Bambha, Tom Reichardt, and Gary Hubbard rounded out the methane detector team.

Measuring automotive emissions

Sandia has been collaborating with the National Research Council, Canada (NRC) and instrument maker Artium Technologies to develop a particulate matter instrument for use in a Portable Emissions System (PEMS). PEMS is intended to check heavy-duty diesel engines for compliance with upcoming EPA and California Air Resources Board (ARB) mandated not-to-exceed (NTE) highway emissions regulations. Engine manufacturers expressed the desire to measure particulate tailpipe emissions to comply with 2007 federal and state emissions restrictions.

The instrument is based on laser-induced incandescence (LII) technology developed by CRF engineer Peter Witze and Greg Smallwood and David Snelling of NRC. LII measures carbon particulate matter in real time. Witze has so far conducted field trials of the system at Cummins Engine and Ford Scientific Research Laboratory, which expressed interest in this technology for engine and aftertreatment system development. Previously, there was no way to measure particulate emissions on board a vehicle in real time.

ARB is now working with the EPA and the Engine Manufacturers Association (EMA) to specify the instruments for the PEMS to be used by the engine manufacturers for NTE compliance. The Artium LII instrument is one of several systems under consideration by the EPA, EMA, and ARB for use by heavy-duty engine manufacturers to verify that their engines meet the requirements of the new regulations.

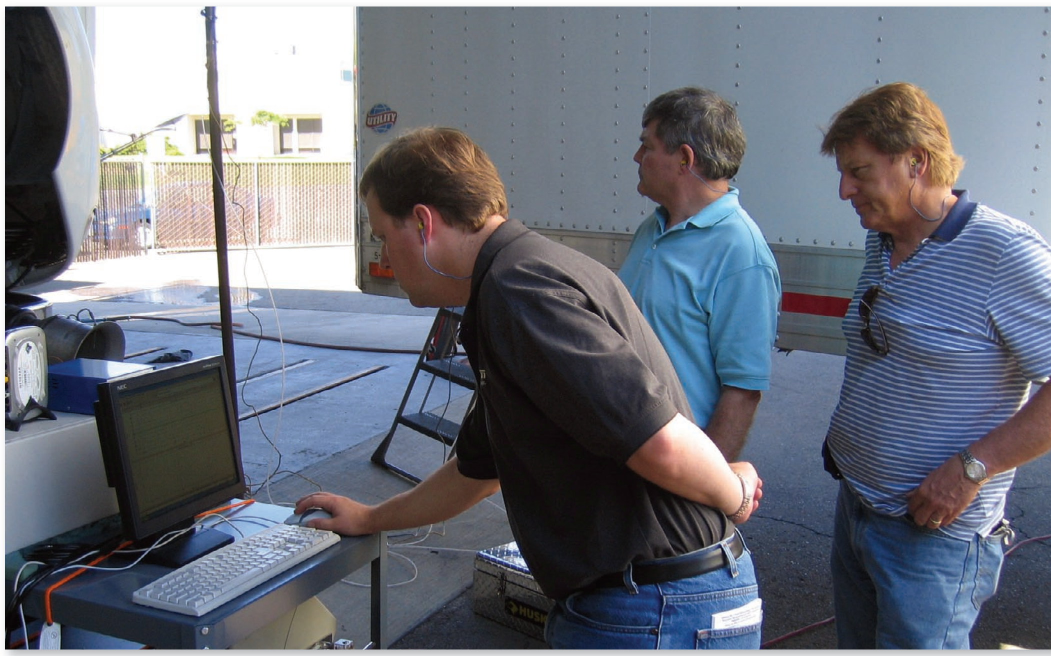
Finding new fuel sources

In the search for renewable alternatives to fossil fuels, fiber cane has emerged as a strong contender, thanks to a Department of Energy (DOE) demonstration project in which CRF researchers played a crucial role.

The DOE project investigated fiber cane as a potential boiler fuel for power generators at the Hawaiian Commercial and Sugar Company (HC&S). To support the project, the Sandia team traveled to Hawaii with a specially designed system, utilizing a laser-induced breakdown spectroscopy (LIBS) probe. The LIBS technique detects chemical elements emitted during the firing process.

HC&S had burned bagasse, the plant residue from sugar processing, to supplement the imported coal and fuel oil that generate steam and electricity for the sugar factory and local electric company. These imported fuels were sufficiently expensive to warrant investigating the possibility of growing cane specifically for biomass-generated power. Fiber cane, used to make fiberboard, showed potential as fuel. But fiber cane still contained the trace alkali metals and other inorganics that were typically leached from sugar cane bagasse during sugar extraction. It was feared that these residues when burned would turn into a sort of glass that would clog boilers, raising maintenance costs and reducing equipment life.

The CRF team of Linda Blevins, Doug Scott, and Howard Johnsen used their special equipment—an intensified charge-coupled device camera, a Nd:YAG laser, and an echelle spectrometer—to collect LIBS data from three fuel combinations: (1) coal, (2) bagasse and coal, and (3) fiber cane, bagasse, and coal. Together with their collaborators from HC&S, the Hawaii Natural Energy Institute, and the University of California, Davis, the Sandians demonstrated that cofiring fiber cane in mixtures with different proportions of other fuels mitigated the fiber cane's tendency to form boiler deposits.



(Left to right) Greg Payne, Artium; Peter Witze, Sandia; and Will Bachelo, Artium, checking emissions using Artium's commercial LII instrument.

These results provide support for fiber cane's potential as a renewable alternative energy source.

Sandia teams also successfully used the LIBS probe to analyze hot gases and particles in other industrial combustion environments, such as black-liquor recovery boilers in paper mills and melting furnaces within the Gallo glass plant in Modesto, CA. Chris Shaddix, Pete Walsh, Alejandro Molina, and Shane Sickafoose contributed to the development and deployment of LIBS in these industrial settings.

Experimental database *(Continued from page 1)*

In soot-containing flame regions, the research team measured gas temperatures via planar two-color pyrometry. To determine the local, time-resolved radiant heat flux from each flame, researchers used a thermopile, a device that measures thermal radiation, with a long, anodized collimation tube. They also measured soot concentrations with planar laser-induced incandescence (LII), calibrated with laser extinction measurements. Figure 2 shows laser-sheet images from steady and pulsed ethylene slot flames.

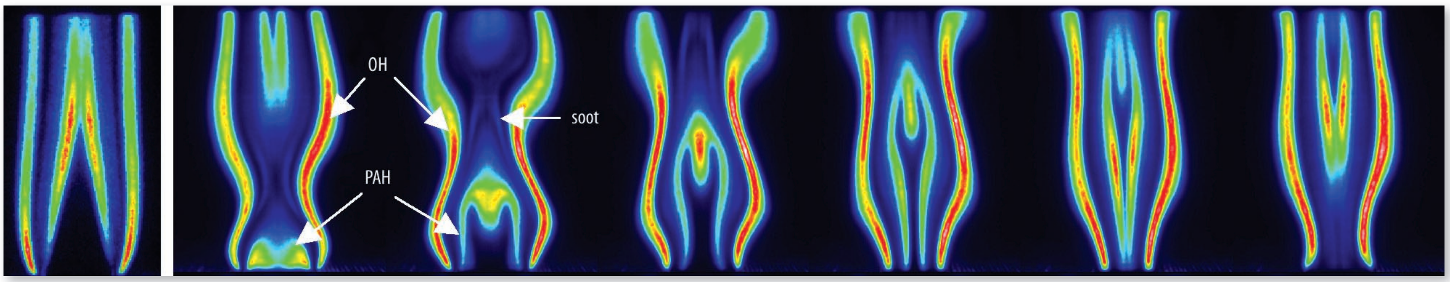


Figure 2. False-color images of LII/PLIF intensity showing the location of OH, PAH, and soot in steady (left) and 15-Hz pulsed (right) normal slot flames of ethylene burning in air. The six consecutive images for the pulsed flame, each separated by 11.1 ms, show the formation and pinch-off of the PAH-containing region of the flame during the pulse cycle.

The primary particle size and aggregate structure of the soot were found through transmission electron microscopy grid sampling with a rapid insertion probe. Finally, researchers used an extractive probe and a gravimetric sampling/light extinction system to determine the local soot dimensionless extinction coefficient (K_e) for each flame.

New insights

These measurements yielded several insights. For example, modulating the fuel flow at approximately twice the natural buoyant instability frequency of the flames results in flame oscillations with a frequency of $f/2$, where f is the forcing frequency. The specific forcing amplitudes and frequencies that trigger this response are fuel-dependent, with methane showing a stronger tendency for $f/2$ behavior than ethylene.

In steady inverse slot flames, the local PAH and soot concentrations as well as the soot radiation are lower than for steady normal flames. In the pulsed flames, however, a vortex roll-up on the fuel-side of the flame sheet results in higher PAH concentrations for the inverse flames.

K_e values for the coannular ethylene and JP-8 flames range from 8 to 10—agreeing with reported postflame measurements—while K_e values for the methane coannular flame and for the slot flames are significantly lower.

A detailed analysis of the database during the next year should yield improved phenomenological understanding and quantitative parameters describing soot formation and radiation in unsteady diffusion flames.

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